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<b>(21) International Application Number:</b> PCT/GB94/02351 <b>(22) International Filing Date:</b> 26 October 1994 (26.10.94)  <b>(30) Priority Data:</b> 9322119.0 27 October 1993 (27.10.93) GB  <b>(71) Applicant (for all designated States except US):</b> ALLIED COLLOIDS LIMITED [GB/GB]; P.O. Box 38, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> JOHNSON, Ian, Michael [GB/GB]; 23 Bankfield Drive, Nabwood, Shipley, West Yorkshire BD18 4AD (GB). COULDWELL, Pauline, Lesley [GB/GB]; 144 Leeds Road, Birstall, Batley, West Yorkshire WF17 0HH (GB).  <b>(74) Agent:</b> GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>
<b>(54) Title:</b> SUPERABSORBENT POLYMERS AND PRODUCTS CONTAINING THEM  <b>(57) Abstract</b>  Particulate superabsorbent polymeric material which is a partially neutralised polymer of an ethylenically unsaturated carboxylic monomer cross linked by a triethylenic or higher ethylenic cross linking agent, preferably tetra allyl ammonium chloride, absorbs above 15 grams, and often above 18 grams, aqueous saline per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre. The polymer preferably has surface cross linking caused by contacting the polymer particles with inorganic and/or covalent cross linking agent for the polymer.		

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**Superabsorbent Polymers and Products containing them**

It is standard practice to provide superabsorbent polymeric material in the form of particles wherein the polymer has been obtained by copolymerisation of  
5 monoethylenically unsaturated carboxylic monomer and polyethylenically unsaturated cross linking agent. The carboxylic monomer groups are usually at least partially neutralised, for instance at least 50% molar in the form of sodium salt.

10 In EP-A-339461 it is proposed to provide such superabsorbent material which can absorb at least 27ml of aqueous saline (as hereinafter defined) per gram of superabsorbent material while under a restraining pressure of at least 21,000 dynes per square centimetre. Aqueous  
15 saline herein is to be understood as being an aqueous solution of sodium chloride containing 0.9 weight % sodium chloride and all absorbency values refer to the absorption of this.

EP 339461 does not describe how those polymers are to  
20 be made and does show that the absorption value tends to drop significantly as the load increases. For instance the absorption at 58,600 dynes per square centimetre in one example is 8g/g compared to a value of 26g/g at 20,700 dynes/cm<sup>2</sup>.

25 In EP 532002 it is proposed to test the absorption under a load provided by a 200 gram weight.

Although these absorption under load tests do give an indication of the ability of the superabsorbent material to absorb urine while under load, such tests indicate only one  
30 of several parameters that can be examined.

Another parameter is the centrifuge retention capacity, which indicates the volume of liquid that the superabsorbent will hold on to under applied pressure. About 200mg of superabsorbent is sealed in a tea-bag of  
35 approx. size 6.35cm x 7.62cm (2.5 inches x 3 inches) and immersed in 0.9% sodium chloride solution for 30 mins. The tea-bag is removed and placed in a basket centrifuge

for 3 mins. at 1600rpm (centrifugal force approx. 250G).  
A tea-bag without polymer is used as the blank.

Centrifuge retention capacity =

5 
$$\frac{\text{wt. of wet polymer} - \text{blank}}{\text{wt. of dry polymer}}$$

Generally for commercial superabsorbents, this value is at least 28 g/g of 0.9 weight % sodium chloride solution.

10 Another parameter is the rewet parameter, which gives an indication of the performance of the polymer when combined with a fibre matrix in a diaper type construction.

Ideally a superabsorbent material would give optimum properties in all these tests, but we have found that known polymers that satisfy the "absorption under load" (AUL)  
15 test of EP 339461 frequently give poor rewet test results.

It would therefore be desirable to be able to provide superabsorbent particulate polymeric material that gives better performance in use and, in particular, such material which complies with a parameter that is a better indication  
20 of overall performance properties.

According to the invention, we now provide a superabsorbent polymeric material which is in the form of particles, wherein

25 the polymeric material has been obtained by copolymerisation of monoethylenically unsaturated carboxylic monomer and a polyethylenically unsaturated cross linking agent having at least three ethylenically unsaturated bonds,

30 the carboxylic groups in the polymer have been at least partially neutralised, and

the particulate material absorbs above 15 grams synthetic urine (i.e., aqueous saline as defined above) per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre.

35 In order that the superabsorbent material has good performance properties in use, these improved "absorption under high load" values should be accompanied by conventional, commercially suitable, centrifuge retention

capacity values of at least about 28g/g and often in the range 29 or 30 up to, for instance, 33 or 34 or in some instances higher, such as up to 36 or more.

5 In order to obtain the improved absorption under load characteristics while maintaining conventional commercial centrifuge retention capacity, it is necessary to optimise the processes of making the particulate superabsorbent material in order to obtain the desired properties. Since there are several variables involved in the production of  
10 superabsorbent particles (including initiation conditions, monomer concentration, choice and amount of cross linking agent and surface cross linking) there are several variables that can be adjusted in order to obtain the required properties. We have found that particularly  
15 useful results are obtained by appropriate selection of cross linking agent, often accompanied by appropriate selection of conditions for surface cross linking.

In this specification, the units and methods of measuring the load are broadly as described in EP 339461, and in particular the load of 63,000 dynes per square  
20 centimetre is obtained by applying a weight of 300 grams over a circular surface area of 2.54cm (1 inch) diameter, i.e., as described on page 7 of EP-A-339461 except that a weight of 300 grams is used instead of 100 grams. In other  
25 units, the load is 6 kilo pascals or 0.9psi.

We also mention herein loads of 21,000 dynes per square centimetre (100 grams over 2.54cm, 0.3psi and 2 kilo pascal) and loads of 42,000 dynes per square centimetre (200 grams over 2.54cm, 4 kilo pascal and 0.6psi).

30 The preferred material absorbs at least 16 and preferably at least 17 grams per gram in 60 minutes under a load of 63,000 dynes per square centimetre. In general values in the range 18 to 28, preferably 20 to 25, g/g in 60 minutes are preferred.

35 We find surprisingly that polymers that are made to meet this absorbency parameter, and optionally other absorbency parameters described below, give much better

performance on other tests such as the rewet test and are, in practice, more effective as superabsorbents for use in diapers and other absorbent articles.

5 The polymers preferably have an absorbency value at a load of 42,000 dynes per square centimetre of at least 18 or 20 and generally at least 22 grams synthetic urine in 60 minutes under this load. Preferred polymers absorb 20 to 28 or 30, generally 20 to 25, grams per gram in 60 minutes under this load.

10 Another useful parameter is the amount of absorption in 10 minutes. Under a load of 21,000 dynes per square centimetre it is preferred that the polymer absorbs at least 15 and preferably at least 20, for instance 18 to 28, grams synthetic urine per gram polymer in 10 minutes.  
15 Under a load of 42,000 dynes per square centimetre it is preferred that the polymer absorbs at least 10 and preferably at least 15, for instance 13 to 25 g/g in 10 minutes. Under a load of 63,000 dynes per square centimetre it is preferred that the polymer absorbs at  
20 least 8 and preferably at least 12, for instance 10 to 20, grams per gram in 10 minutes.

Surprisingly, the absorbency in 60 minutes under a load of 21,000 dynes per square centimetre (i.e., the value in the test described in EP-A-339461) does not seem  
25 particularly critical. Although useful polymers for use in the invention can have the absorbency of at least 27g/g at 21 dynes per square centimetre proposed in EP 339461, it is also possible in the invention to obtain excellent results under higher loads, and excellent performance in  
30 practice, even though the absorbency over 60 minutes at 21,000 dynes per square centimetre is below 27g/g, for instance it may be in the range 20 to 26g/g.

The polymer is made by copolymerisation of  
monoethylenically unsaturated carboxylic monomer with  
35 polyethylenically unsaturated cross linking agent. Polymerisation processes of this general type are well known in the literature for making superabsorbent polymers

but conventional techniques have not produced the polymers now being defined. For instance a conventional polymerisation comprises aqueous polymerisation of partially neutralised acrylic acid in the presence of a difunctional cross linking agent such as methylene bis acrylamide. This gives inadequate properties, according to our new tests, and the properties are inadequate even when the resultant particles are subjected to surface cross linking by one of the generally known techniques.

A wide range of cross linking agents have been proposed in the literature including various tri-functional and tetra-functional and higher functional cross linkers. Usually the tri-functional and tetra-functional cross linking agents have no more than two ethylenically unsaturated bonds substituted on to a single atom. For instance tetra-allyl butane diamine is mentioned as an example in WO91/18031 and this has two allyl groups substituted on to one amino nitrogen atom and two allyl groups substituted on to another amino nitrogen atom. The same disclosure also mentions, for instance, triallylamine, wherein all three allyl groups are substituted on to the same amino nitrogen atom. Blends of triallylamine with methylene bis acrylamide or other cross linkers are also exemplified.

In the invention we find that it is important that at least half, and preferably substantially all, the cross linking agent used in the copolymerisation is provided by a material which has at least three ethylenically unsaturated bonds, preferably substituted on to a single atom. For instance it may have at least three allyl or other ethylenically unsaturated groups substituted on to a single atom, usually an amino nitrogen atom. We believe that this close proximity of the ethylenic unsaturation contributes to the formation of a gel structure in the polymer that in turn contributes to the defined absorption properties. Preferably at least half of the polyethylenically unsaturated cross linking agent has at

least four of the ethylenically unsaturated bonds, preferably on to a single atom. Thus preferred cross linkers are triallylamine and, especially, tetra-allyl ammonium compounds.

5        Although the copolymerisation can be conducted on the free acid monomer followed by partial or complete neutralisation, it is preferred that the polymerisation is conducted on partially neutralised monomer or even wholly neutralised monomer, e.g., acrylic acid-sodium acrylate  
10       blends. Since it is preferred that the cross linking agent should be soluble in the aqueous polymerisation medium the polyethylenically unsaturated cross linking agent should be water soluble, and it is therefore preferred that the cross linking agent should be an acid  
15       addition (e.g., triallylamine hydrochloride) or quaternary ammonium salt.

      The preferred cross linkers are quaternary ammonium salts of triallylamine, for instance the metho sulphate, methyl chloride, methyl bromide or methyl iodide salt of  
20       triallylamine or, preferably, the allyl chloride or other allyl quaternary salt of triallylamine. The preferred cross linker is tetra-allyl ammonium chloride. Although it can be used in combination with other cross linkers, such as triallyl ammonium metho sulphate, preferably it is  
25       used as the only cross linker.

      The amount of cross linker may be selected within the conventional range, for instance 0.05 to 3%, often around 1 or 1.5%.

      The monoethylenically unsaturated carboxylic monomer  
30       is generally acrylic acid but can be any of the other conventional carboxylic monomers. It can be copolymerised with other water soluble monomers but generally the polymer is a homopolymer of acrylic acid. The degree of neutralisation of the carboxylic groups during  
35       polymerisation or in the final polymer (for instance as a result of treating the polymer with sodium hydroxide or other alkali) is usually at least 50% and generally at



least 70%. It is generally unnecessary for it to be above 90%.

The polymerisation should be initiated using an initiator system that will contribute to the formation of the desired gel properties. This can involve a thermal system or a redox system or a mixture, but we find satisfactory results are obtained by use of a combination of a reducing agent such as sodium sulphite with an oxidising agent such as a peroxy compound, especially tertiary butyl hydrogen peroxide.

The polymerisation is generally conducted on aqueous monomer solution having a monomer content in the range 25 to 60%, generally 25 to 40%, often around 25 to 35%.

The polymerisation can be conducted as a reverse phase bead polymerisation in a water immiscible liquid in known manner, to give an appropriate particle size, or the resultant particles may be comminuted. Preferably, however, the polymerisation is conducted as a bulk gel polymerisation and is followed by comminution and drying in conventional manner.

The particle size is generally above 100 microns and below 1mm. Preferably it is above about 200 or 300 $\mu$ m. Preferably it is not more than about 600 or 700 $\mu$ m. A range of 300 to 600 $\mu$ m is suitable.

It is generally preferred to subject the particles to a surface cross linking treatment, as a result of which the cross linking density in the surface of the particles is greater than in the central parts of the particles. Techniques of surface cross linking preformed superabsorbent particles are known in the literature and, when the particles are being made by reverse phase polymerisation, it is also known to be able to surface cross link them during their formation or prior to recovery from the reverse phase system.

The surface cross linking may be brought about by contact of the surfaces with an inorganic cross linking

agent, for instance aluminium sulphate, sodium aluminate or other polyvalent metal compound.

Preferably, however, some or all of the cross linking is by reaction with a material that reacts covalently with the polymer, for instance a silane coupling agent (for instance as described in EP 195406) or a glycidyl ether or other epoxy or other material capable of reacting with the carboxylic groups in the polymer. For disclosures of surface cross linking mechanisms reference may be made to, for instance, EP 317106, 503268, 386897, U.S 5,053,460 and U.S. 4,587,308.

The surface cross linking effect may be supplemented by, treating the surface with finely divided silica such as Aerosil or Sipernat (trade marks). Typically this is applied as a slurry. For instance the particles may be contacted with an aqueous composition containing not more than 10 or 15% of finely divided silica. If desired, the particles may be treated sequentially by aqueous inorganic cross linking agent, aqueous organic cross linking agent and aqueous silica, in any order, or two or more of them may be applied in a single coating composition.

The surface cross linking can be achieved merely by, for instance, spraying the particles, generally while entrained in air, with a dilute solution of a cross linking agent, wherein the solution preferably contains both a covalent cross linking agent and silica. However any other convenient method of contacting the particles with the surface cross linking agents can be used. Often the treated particles are then heat treated for instance to a temperature of 50 to 200°C, e.g., 80 to 120°C, for five minutes to an hour or whatever time is appropriate for optimum results.

In order to promote the surface cross linking in such a way as to maximise the "absorption under high load" value in accordance with the invention, it can be desirable to take steps to control the penetration of the surface cross linking agent into the structure of the particulate

material. To control penetration, it can be desirable to adjust the concentration of the cross linking agent in a dilute aqueous solution that is used for the contact. Preferably the surface cross linking is performed by  
5 contacting the particles with an aqueous solution containing less than 25% cross linking agent, preferably less than 10% cross linking agent, for instance 1 to 10%. It may contain less than 5% cross linking agent, for instance 0.5 to 5%.

10 It can be desirable to provide both ionic and covalent cross linking. The particles may be contacted sequentially with aqueous solutions of covalent and ionic cross linking agents or they may be contacted with a single solution containing both cross linking agents dissolved in  
15 it.

The amount of cross linker solution that is applied is generally such that the particles absorb 0.01 to 2% of each cross linker, generally 0.1 to 1%, often greater than 0.2 or 0.5%, of total cross linker.

20 Although satisfactory results are generally obtained merely by surface cross linking the individual particles, good results can also be obtained by agglomerating the particles wherein the agglomeration is caused by contacting the superabsorbent particles with the aqueous cross linking  
25 agent (generally including silica) under conditions that the particles agglomerate, followed by drying the agglomerates.

If desired, the agglomerates may be subjected to comminution to reduce them to the desired final particle  
30 size.

By appropriate selection of the polymerisable monomer or monomers, the cross linking agent or cross linking agents, the initiator and other polymerisation conditions, the particle size, optional surface cross linking  
35 (including selection of the epoxy or other cross linking agent and usually silica) and optional agglomeration with

a cross linking agent, it is easily possible to obtain novel polymers having the defined parameters.

Best results are obtained by polymerising partially neutralised acrylic acid using tetra-allyl ammonium chloride as cross linker and a redox system such as sulphite-peroxide, followed by surface cross linking using a dilute aqueous solution of a glycidyl ether or other covalent cross linking agent, preferably in combination with finely divided silica and/or a dilute aqueous solution of aluminium salt.

The following is an example of a preferred synthesis of the novel polymer:

Example 1

221g of 46% aqueous sodium hydroxide is added to 244g glacial acrylic acid and 435g distilled water to form 1,000g of a 75% neutralised 30% solids sodium acrylate solution. This is de-oxygenated with nitrogen. 2mls of a 60% w/v aqueous solution of ethylene diamine tetra-acetic acid is then added followed by 3.3mls of a 45% w/v aqueous solution of tetra-allyl ammonium chloride.

Polymerisation is then initiated by the addition of 0.9mls of 0.5% w/v aqueous solution of sodium sulphite followed by 0.45mls of a 0.5% w/v aqueous solution of tertiary butyl hydrogen peroxide.

Polymerisation is allowed to go to completion. The resultant gel is then comminuted and dried in an oven and ground to the selected particle size, typically such that as much as possible is between 300 and 600 $\mu$ m.

A dispersion is formed of 7.5% ethylene glycol diglycidyl ether and 7.5% finely divided silica and 85% by water. This is sprayed on to the particles to give a dry pick-up of 1% of each cross linking agent, based on the weight of the particles. The particles are then redried.

The particles obtained after the surface cross linking are described as product A.

In another test, the process is repeated using triallyl methyl ammonium metho sulphate as the cross

linking agent and D is the polymer obtained using triallyl methyl ammonium metho sulphate as the cross linking agent with surface cross linking as in the example.

The centrifuge retention capacity (CRC) and absorbency under load after 60 minutes at loads of 100, 200 and 300g are recorded for products A and D and for products E to K as shown in the following table:

	Sample	Absorbency under load			CRC
		100g	200g	300g	
10	A	27	22	16	34
	D	26	19	15	31
	E	29	10	8	33
	F	23	13	7	30
15	G	21	9	9	31
	I	-	-	11	29
	J	-	-	10	28
	K	-	-	8	29

E, F and G are commercially available superabsorbent polymers. I, J and K are polymers obtained used methylene bis acrylamide as the cross linking agent in various amounts but without surface cross linking. When methylene bis acrylamide is used with surface cross linking the values are lifted by only a small amount.

The clear benefit of the polymers defined in the invention (A and D, and preferably the tetra-allyl, surface cross linked polymer A) is apparent.

#### Example 2

A process broadly as described in Example 1 for the production of product D is conducted except that the cross linker is about 0.6% (based on monomer) tetra allyl ammonium chloride, the initiator is a ferric salt, ascorbic acid, hydrogen peroxide, sodium persulphate initiator and the final particles were each coated with 3% solutions of ethylene glycol diglycidyl ether, aluminium sulphate and Sipernat 22S silica to give a pick-up of 0.4% of each. The resultant product had CRC 32g/g, and absorption under load values of 28 and 20g/g at loads of 100 and 300g respectively.

The novel polymers are preferably incorporated into absorbent structures such as diapers, sanitary pads,

tissues and other fibrous materials, in conventional manner, for instance as described in EP-A-339461. These absorbent materials may be incorporated into diapers including topsheet, backsheet and appropriate fastenings, all in conventional manner.

It is not possible to define a standardised rewet test since even quite small differences in the details of the absorbent structure in which the superabsorbent particles are incorporated will tend to give slightly different values. However, provided the same absorbent structure is used, comparative rewet tests are valuable.

In our rewet tests, 5g of polymer are scattered between two layers of fluff and the rewet values are then compared under different loadings, being subjected to first, second and third rewets in conventional manner. Product A and a commercial product were tested by this test and the results are set out in Table 2 below.

		<u>Table 2</u>			
		test	1st	2nd	3rd
20	Product A	absorption	32	36	60
		time (secs)			
	5 kilo wt.	rewet mls.	0.4	6.8	7.7
25	Product A	absorption	32	48	62
		time (secs)			
	10 kilo wt.	rewet mls.	2.6	6.8	11.5
30	Commercial product	absorption	34	65	80
		time (secs)			
	5 kilo wt.	rewet mls.	1.7	6.3	11.8
	Commercial product	absorption	35	72	103
		time (secs)			
35	10 kilo wt.	rewet mls.	4.5	8.2	14.2

The clear benefit of product A, compared to the commercial product, is apparent from these values. The rewet value should be as low as possible as should the absorption time. The invention also includes polymers in fibre form and polymers having the specified absorption values which can be cross linked graft polymers.

Preferably all the polymers of the invention have a low content of extractables.

CLAIMS

1. A superabsorbent polymeric material which is in the form of particles, wherein  
the polymeric material has been obtained by  
5 copolymerisation of monoethylenically unsaturated carboxylic monomer and a polyethylenically unsaturated cross linking agent having at least three ethylenically unsaturated bonds,  
the carboxylic groups in the polymer have been at  
10 least partially neutralised, and  
the particulate material absorbs above 15 grams aqueous saline per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre.
2. A polymeric material according to claim 1 having a  
15 centrifuge retention capacity of at least 28 grams aqueous saline per gram polymeric material.
3. A polymeric material according to claim 1 or claim 2 which absorbs at least 17 grams aqueous saline per gram polymeric material in 60 minutes under a load of 63,000  
20 dynes per square centimetre.
4. A polymeric material according to claim 1 or claim 2 which absorbs at least 18 to 28 grams aqueous saline per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre.
- 25 5. A polymeric material according to claim 1 or claim 2 which absorbs at least 20 to 25 grams aqueous saline per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre.
6. Polymeric material according to any preceding claim in  
30 which the cross linking agent has at least three allyl groups substituted on to a single atom.
7. A polymeric material according to any preceding claim in which the cross linking agent has at least four ethylenically unsaturated groups.
- 35 8. A polymeric material according to any preceding claim in which the cross linking agent is selected from triallyl



amine and acid addition and quaternary ammonium salts thereof.

9. A polymeric material according to any preceding claim in which the cross linking agent is tetra allyl ammonium chloride, bromide or iodide.

10. A polymeric material according to any preceding claim in which the particles have been provided with surface cross linking by contacting the particles with an aqueous composition containing not more than 10% by weight of cross linking agents selected from inorganic cross linking agents and cross linking agents that react covalently with carboxylic groups in the polymer.

11. An absorbent structure which is a diaper, sanitary pad or tissue incorporating absorbent polymeric material according to any preceding claim.

## AMENDED CLAIMS

[received by the International Bureau on 04 April 1995 (04.04.95);  
original claims 2-11 replaced by amended claims 2-15;  
original claim 1 unchanged (2 pages)]

1. A superabsorbent polymeric material which is in the form of particles, wherein

5 the polymeric material has been obtained by copolymerisation of monoethylenically unsaturated carboxylic monomer and a polyethylenically unsaturated cross linking agent having at least three ethylenically unsaturated bonds,

10 the carboxylic groups in the polymer have been at least partially neutralised, and

the particulate material absorbs above 15 grams aqueous saline per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre.

2. A polymeric material according to claim 1 in which

15 (a) the polymeric material has been made using as the cross linking agent a polyethylenically unsaturated cross linking agent having at least four ethylenically unsaturated bonds and/or

20 (b) the particles have been provided with surface cross linking by contacting the particles with an aqueous composition containing not more than 25% by weight of cross linking agent selected from inorganic cross linking agents and cross linking agents that react covalently with carboxylic groups in the polymer and heat treating the  
25 particles at a temperature of 50 to 120°C.

3. A polymeric material according to claim 2 having a centrifuge retention capacity of at least 28 grams aqueous saline per gram polymeric material.

4. A polymeric material according to claim 2 or claim 3  
30 which absorbs at least 17 grams aqueous saline per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre.

5. A polymeric material according to claim 2 or claim 3  
35 which absorbs at least 18 to 28 grams aqueous saline per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre.

6. A polymeric material according to claim 2 or claim 3 which absorbs at least 20 to 25 grams aqueous saline per gram polymeric material in 60 minutes under a load of 63,000 dynes per square centimetre.
- 5 7. Polymeric material according to any of claims 2 to 6 in which the cross linking agent has at least three allyl groups substituted on to a single atom.
8. A polymeric material according to any of claims 2 to 7 which has been made using the said cross linking agent
- 10 having at least four ethylenically unsaturated bonds and in which the particles have been provided with the said surface cross linking.
9. A polymeric material according to any of claims 2 to 8 in which the polyethylenic cross linking agent is
- 15 selected from triallyl amine and acid addition and quaternary ammonium salts thereof.
10. A polymeric material according to any of claims 2 to 9 in which the polyethylenic cross linking agent is tetra allyl ammonium chloride, bromide or iodide.
- 20 11. A polymeric material according to any of claims 2 to 10 in which the aqueous composition contains not more than 10% by weight of the cross linking agent.
12. A composition according to any of claims 2 to 11 in which the aqueous composition contains glycidyl ether as
- 25 cross linking agent.
13. A composition according to any of claims 2 to 12 in which the aqueous composition also contains silica.
14. A composition according to any of claims 2 to 13 in which the aqueous composition contains ethylene glycol
- 30 diglycidyl ether and silica.
15. An absorbent structure which is a diaper, sanitary pad or tissue incorporating absorbent polymeric material according to any preceding claim.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 94/02351

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C08F220/04 A61L15/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08F A61L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,94 15651 (CHEMISCHE FABRIK STOCKHAUSEN) 21 July 1994 see abstract; claims; table 3	1-6,8, 10,11
A	WO,A,92 00108 (CHEMISCHE FABRIK STOCKHAUSEN) 9 January 1992 see abstract; claims; examples see page 7, paragraph 3	1-11
A	EP,A,0 530 438 (HOECHST CELANESE) 10 March 1993 see abstract; claims; example see page 3, paragraph 1	1-11
<input type="checkbox"/> Further documents are listed in the continuation of box C. <span style="margin-left: 100px;"><input checked="" type="checkbox"/> Patent family members are listed in annex.</span>		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"B" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-weight: bold;">23 January 1995</div>		Date of mailing of the international search report  <div style="text-align: center; font-weight: bold;">10. 02. 95</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-weight: bold;">Mettler, R-M</div>

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PCT/GB 94/02351

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